

Conventional sintering of LAS-SiC nanocomposites with very low thermal expansion coefficient

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Abstract.

Very low thermal expansion materials have been developed in a wide temperature range from -150 °C to 450 °C. These very low expansion materials are composed of a lithium aluminosilicate matrix with dispersed silicon carbide nanoparticles. The nSiC content in the most stable composite has resulted to be 27 vol.%. Powder processing and sintering temperature control have been found to be of key importance in order to obtain low porosity sintered nanocomposites. Here it is proposed the sintering by pressureless methods (conventional sintering) in order to obtain a LAS-nSiC nanocomposite with improved mechanical properties and excellent expansion behaviour by means of control of the phase reactions and glass formation during sintering.

Keywords. Sintering, nanocomposites, thermal expansion, lithium aluminosilicates.

1. Introduction.

Materials with very low thermal expansion coefficient (CTE) have a wide range of applications in very different fields. These materials are required in many types of precision devices and in instrumental equipments of high technology systems, from the microelectronic industry to precision optics. In summary, in all those uses in which dimensional stability with changes in temperature of any precision element is required, it will be necessary to lower the material's CTE which form those elements.

Tailor made CTE materials can be design making composites which combine phases with positive and negative CTE. The lithium aluminosilicate (LAS) system is frequently used with this purpose in very different uses, from cook tops glass- ceramics to satellite mirrors in aerospace telescopes. Some phases of this family have negative expansion coefficient and are used in composites with tailored CTE. However, materials with negative CTE often have low fracture strength due to the strong anisotropy between the different crystallographic orientations, in which it is common to find the negative behaviour in one direction and positive in the others. This anisotropy causes microcracking which results in low values for the mechanical properties of these materials. Nevertheless, the usefulness of these expansion properties for the fabrication of very low CTE composites has a wide potential in many fields in engineering, photonics, electronics and certain structural applications [1]. The negative expansion phase in the LAS system is β - eucryptite (LiAlSiO_4), due to the large negative expansion in the one of its crystallographic directions. Spodumene ($\text{LiAlSi}_2\text{O}_6$) and petalite ($\text{LiAlSi}_4\text{O}_{10}$) have close to zero CTE.

The traditional method of fabrication of LAS materials is the glass processing to produce glass- ceramics. This method allows the CTE control by the crystallization of LAS phases from a melt phase obtaining a glass- ceramic at lower temperatures with adjusted CTE [2]. Frequently, this method requires a highly controlled and complicated processing in order to avoid heterogeneities. In addition, as consequence of the high amount of glass phase, the mechanical properties are relatively poor (in comparison with other ceramic materials) which make these materials unsuitable for certain industrial applications, for example, some satellite mirror blanks. This is the case of Zerodur ® very often used in many applications, included satellite mirror blanks, but with too low fracture strength and elastic modulus values. New requirements in the dimensions and uses of satellite mirrors make the properties of glass-ceramic materials insufficient to fulfil properties needed during launch and use of satellites. Therefore, it is necessary an alternative to the glass- ceramic materials in order to improve their mechanical properties. There are other materials with better mechanical performance than glass-ceramics, as cordierite ceramics and Invar ® but their properties (thermal and mechanical) can still be improved. The design of composites with very low CTE using negative LAS matrix with addition of second phases with positive CTE, as the materials described in [3-7], seems to be a promising alternative. This option is very interesting as together with the CTE design for a certain temperature range, also other properties can be design, adding the proper amount and type of second phases in the matrix. This has been tested successfully in [6] where they have obtained a zero expansion material at room temperature with high elasticity for a LAS-SiC composite similar to the one proposed in our study. In that study, it was reported the influence of the silicon nitride addition on the sinterability of LAS-SiC composites which resulted in close to

theoretical density materials with excellent thermal and mechanical properties. In the other side, a lot of work has been done in the SiC/LAS composites using SiC fibres and whiskers [8-14] and in most of them the LAS matrix is a glass-ceramic. From those studies one can realize that there are great difficulties to densify such composites, the processing methods are not simple and frequently it is need to sinter the materials by pressure assisted methods.

It is well known that the sintering of LAS materials to obtain dense ceramic bodies is quite complicated[15]. This is due to their narrow range of sintering temperatures and the easy formation of vitreous phase as the invariant points in this system are found at relatively low temperatures[16]. The large difference between the sintering temperatures of LAS phases and SiC make it even more difficult to obtain dense bodies of this type of composites in the solid state.

In the present study we have examined the way of obtaining a LAS/SiC nanocomposite by conventional sintering in inert atmosphere without sintering aids, by a simple fabrication method which allows the production of large pieces with complex shapes (impossible to obtain by pressure assisted methods). The sintering will be adjusted trying to avoid the presence of glass phase in order to obtain a very low CTE material in a wide temperature range (not only at room temperature) with improved mechanical properties. The processing method and the control of the microstructure are the key points to develop such nanocomposites together with a fine temperature control during sintering.

2. Experimental Procedure.

β -eucryptite solid solution powders with a composition 1: 1.0009: 3.109 of $\text{LiO}_2\text{:Al}_2\text{O}_3\text{:SiO}_2$ has been synthesized by the method proposed in a previous study [17]. The synthesis is based on blending kaolinite with lithium carbonate and tetraethylorthosilicate. The LAS powders so synthesized have a mean grain size of 1 μm and they have been characterized for their CTE behaviour as described in [17]. Negative CTE values of the LAS sintered samples have been used to design composites with very low expansion in a wide temperature range taking into account the estimated final sintering temperature of the nanocomposite. As it has been shown in [17], there is a relation of the CTE with the sintering temperature. The CTE of the LAS phase used in this study becomes more negative at higher sintering temperatures. This has to be taken into account in the design of a composite where there are second phases in different amounts which will change the final sintering temperature of the composite itself. The SiC powders used to prepare the very low CTE composite are commercial nano-SiC powders from Hubei with a mean grain size below 100 nm. Sintered n-SiC has also been characterized to obtain a CTE value in order to design the very low CTE composite. Different proportions of LAS-nSiC have been tested in order to obtain a very low thermal expansion composite in the temperature range of $-150\text{ }^\circ\text{C}$ to $+150\text{ }^\circ\text{C}$. The mixtures were made in ethanol under mechanical stirring (ball milling) for 60 minutes. After that, some samples have been homogenized and milled by high energy attrition mill at 300 r.p.m during 60 minutes. Both dispersions were dried at $100\text{ }^\circ\text{C}$ overnight and the obtained powders were sieved under 63 μm . The powders were isostatically pressed (200 MPa) into small cylinders. The conformed materials were sintered in Ar atmosphere at temperatures between 1300 and 1400 $^\circ\text{C}$ with a ramp of $300\text{ }^\circ\text{C/h}$ and 2 hours of dwell time.

The sintered samples were ground into powder to study the phase composition by XRD with a diffractometer SIEMENS[®] (D 5000), with “Bragg-Brentano” geometry and Cu k_α radiation at 40 kV and 30 mA ($\lambda = 0.15418$ nm).

Samples were cut, polished and Au coated to observe the microstructures with a SEM Zeiss DSM 950. Densities were measured by He picnometry for theoretical density and by Archimedes method for apparent density. The Young modulus has been estimated from measurements of the resonance frequency by a Grindosonic instrument and the fracture strength was calculated by the four- point method with 3x4x50 mm polished surface bars in an Instron 8562 apparatus. Finally, a Netzsch DIL402C dilatometer was used to measure the elongation of the sintered samples and the dynamic sintering of pressed green bars.

3. Results and discussion.

3.1. Choosing a very low CTE composition.

The law of mixtures has been applied to design the very low thermal expansion coefficient composite in the temperature range of -150 °C to +150 °C. Nevertheless, experimental results for a wider temperature interval are shown, up to +450 °C (Figure 1). For the temperature range of -150 °C to +150 °C, the CTE values of the LAS and SiC sintered materials are -2.90 and $2.38 \times 10^{-6} \text{ K}^{-1}$ respectively. The law of mixture didn't succeed to give a zero expansion composite. Composites with the following volume percentage of LAS-SiC have been prepared and sintered at 1300 °C: 95/5, 83/17, 73/27 and 70/30. With this first test we aimed to choose the closest to zero CTE composition in order to make a deeper sintering study afterwards.

Dilatometries in the temperature range of -150 °C to +450 °C show the expansion behaviour of these composites as illustrated in Figure 1. The temperature reference for the dilatometric tests is room temperature. The LAS/SiC composite with composition 73/27 is the one that shows the more stable curve (with the less steep elongation curve). Composition 70/30 also gives a low absolute expansion but have a steeper slope at high temperatures. The CTE value of the composite 73/27 is very low ($-0.28 \times 10^{-6} \text{ K}^{-1}$ in -150 °C to +150 °C and $0.32 \times 10^{-6} \text{ K}^{-1}$ in -150 °C to +450 °C). This composition has been chosen for the sintering study that is described below. In order to obtain low porosity composites with improved thermal and mechanical properties it was carried out a study of the sintering conditions for the sample with the composition LAS/nSiC 73/27 vol.%.

3.2. Sintering study(?)

The following sintering study has been performed in order to obtain high density composites without sintering aid components and by means of pressureless sintering methods. It is important to focus on sintering process in the solid state, as the presence of glassy phase can have strong effects on the elastic and thermal properties of the composite. For applications such as satellite mirrors, it is also relevant that the final material would be highly homogeneous in order to have a final polished surface free of heterogeneities for a high quality optical surface, so both, porosity and glass, should be minimized to fulfil this requirement.

The processing method of the powders has result also relevant in order to achieve highly homogeneous materials. Figure 2 shows the results of two sintered samples with the same composition but processed by two different methods. Sample of Figure 2a was processed by ball milling, and high energy attrition milling was used in sample of

Figure 2b. It can be observed how the high energy attrition milling yields to more homogeneous materials with lower porosity. Tests of processing with ordinary attrition milling have been performed and results were similar to those of ball milling, with insufficiently homogeneous materials. These two process methods, ball and attrition (not high energy) milling are very commonly used in ceramic processing and have shown to be unsatisfactory to produce homogeneous powders for this composite.

The second essential point for the LAS-nSiC nanocomposites sintering is the temperature control. Figure 3 shows the dynamic sintering curves for both, the LAS matrix used in the composite, and the LAS-nSiC composite itself in argon atmosphere. Sintering of both samples starts at around 900 °C. For the LAS sample, the slope of the curve dramatically changes at around 1350 °C where the sample seems to start melting. For the LAS-nSiC sample it can be observed that the slope of the curve smooths down at around 950 °C up to 1210 °C probably due to densification impediment caused by the SiC phase nanoparticles. Densification takes place in solid state and must be related to grain boundary diffusion. The presence of second phases slows down this mechanism as it is discussed below. Over 1210 °C the slope changes again as a consequence of the matrix contraction at higher temperatures. According to these curves it is not possible to obtain high density sintered LAS-nSiC nanocomposites in the solid state. The key point in order to obtain higher density LAS-nSiC nanocomposites will be adjusting the sintering temperature maintaining a dwell time long enough.

The effect of SiC addition to the LAS matrix, as we have seen from the dynamic sintering test, is to raise the sintering temperature of the composite compared to the LAS matrix sintering temperature. This is in well agreement with the melting points

reported in [6] for the LAS matrix (1417 °C) and for the LAS-20%SiC composite (1416 °C). The addition of 20% SiC to the LAS matrix doesn't affect the melting point (only 1 °C). The melting point for the LAS phase used in our study is sensibly lower as observed by dilatometry and estimated by thermodynamic calculations using the software MTDATA [18], which gives a *solidus* temperature for this LAS composition of 1388.8 °C and a *liquidus* temperature of 1415.4 °C. If the melting point of the matrix and the composite is very similar, and as we have pointed out, the densification takes place in the solid state, the sintering temperature should be the same. But this is not the case, and it is well known the difficulty to obtain dense LAS-SiC composites without additives [6], (which low the sintering temperature by the formation of a glass phase), and with pressureless methods. The explanation is that SiC nanoparticles, which are situated at the LAS grain boundaries, have a high melting point (~2700 °C) and, consequently, a very low diffusion capability at the sintering temperatures we are dealing with (< 1400 °C). For this reason, SiC nanoparticles hinder the densification of the LAS matrix by means of impeding diffusion between the LAS grains in the matrix. Figure 4 shows the microstructure where the nSiC particles are distributed around the LAS grains producing this impeding effect.

According to this, and in order to obtain high density materials with the lowest glass phase amount there have been tried different sintering temperatures with 2 hours dwell time and the material's properties were evaluated.

Using high enough temperatures to obtain dense bodies but controlling the glass formation is possible thanks to the chemical stability of the used LAS phase at such high temperatures for the LAS system [16-17].

Figure 5 shows the diffractograms of the starting powder and one of the sintered samples chosen as an example as all the samples show the same result: there is no reaction between β - eucryptite and SiC and the same diffraction pattern can be observed before and after sintering. The control on the LAS stability and the glass formation allow us to perform several sintering cycles from 1350 °C to 1400 °C. Densities vary from 77 to 95 % of the theoretical density in this temperature range. Results are depicted in Table 1 for the sintering cycles between 1350 and 1390 °C as the 1400 °C sintered sample suffered catastrophic melting. This is in agreement with the thermodynamic estimations of the glass phase formation in the LAS matrix. We have mentioned that the estimated solidus temperature is 1388.8 °C, so the first liquids are not formed in the sintered samples between 1350 and 1380 °C. The sample sintered at 1390 °C (very close to the estimated solidus) must have some glass phase, but the estimated amount of glass phase formed at this temperature is very low, as can be seen in Figure 6. The slope of the amount of liquid formed with temperature show an important increase at around 1407 °C, so the amount of glass phase present at lower temperatures is very low at 1390 °C.

3.3. *Thermal expansion.*

The elongation behaviour of the sintered samples can be observed in Figure 7 for a temperature range between -150 °C and 450 °C. All the samples show negative expansion behaviour for the low temperature range up to approximately 100 °C and then change to positive up to 450 °C. Nevertheless the variation is very small and the coefficient of thermal expansion of all the studied samples is below $0.1 \times 10^{-6} \text{ K}^{-1}$ in absolute value for the whole temperature range and they can be defined as very low thermal expansion materials. Detailed data of the alpha values can be observed in Table

1. These results in the expansion properties of the composites are very important for applications where the materials need to exhibit very low expansion in a wide temperature range, for example in telescope mirrors for satellites, where the temperature differences can be as high as -150 °C to 50 °C or even higher. These composites are good candidates for this technology as they fulfil the thermal requirements, and the mechanical properties that they exhibit are good compared with materials which are now used in this application, such as Zerodur ®.

The low amount of glass phase formed, as discussed above, together with the relatively high density of the sintered materials and the excellent thermal properties make these materials good candidates to be used in technologies where highly homogeneous and ultrastable thermal properties are required. It has to be said that the elastic properties are still low for some applications as the density of the samples is still below the theoretical density values (95%). Post-HIP treatments on the sintered can be applied to improve this density and consequently, the elastic modulus of the samples. Table 1 shows the values of the Young's modulus and it can be seen that they are below the theoretical values which would be around 150-165 GPa, and also below the 150 GPa reported in [6] for a LAS-SiC composite with added Si₃N₄. Nevertheless, our results go beyond the elastic properties of the most commonly material now in use in the satellite mirror industry, Zerodur ® with a Young's modulus of 90 GPa. Also the fracture strength is higher than that of LAS ceramics and glass-ceramics [19] which is between 15-30 MPa.

In summary, the values of elastic modulus, fracture strength and density increase with increasing temperature up to 1390 °C. Thermal expansion slightly increases from 1380 to 1390 °C. Specific rigidity values over 40 GPa/g/cm³ are reached for the highest

temperatures which is in good agreement with other values other LAS-SiC composites [3] and can be improved either using sintering aids[6], which can affect the homogeneity properties, or by post-HIP treatments. Also, improving the final density by post-HIP treatments could yield even better values for the mechanical properties with controlled glass phase formation during the treatment. In this work it has been shown that it is possible to obtain a very low thermal expansion material in a wide temperature range with improved mechanical properties and that it can be produced by pressureless sintering methods. These methods open the possibility of obtaining large sintered bodies with complex shapes which are much more difficult or even impossible to obtain by pressure assisted methods.

4. Conclusions.

High energy attrition milling of LAS-nSiC powders produce fine and homogeneous mixtures which can be densify to relatively high density values by pressureless or conventional sintering methods without additives. These relatively dense bodies are composed of β - eucryptite and SiC after sintering with very low amounts of glass phases. Densities can be improved by post-HIP treatments. The expansion behaviour of the sintered bodies show very low alpha values for a wide temperature range including cryogenic conditions which is essential for some applications such as satellite mirror blanks. The so obtained materials have improved mechanical properties and higher Young modulus compared with other very low CTE materials used in such applications. The conventional sintering methods used open the possibility of large and complex shaped pieces that are otherwise difficult to obtain by pressure assisted sintering methods. The achieved low amount of glass phase formed during sintering, improve the

homogeneity of the composites. All these material's properties makes them suitable for a wide range of applications like telescope mirrors and other applications in optics and electronics, as well as the mentioned satellite mirror blanks.

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Figure 1. Expansion versus temperature of the LAS-nSiC sintered materials tested to adjust the CTE value.

Figure 2. SEM microphotographs. a and b are polished sections of the same LAS-nSiC composition mechanically mixed and high attrition milled respectively. The same magnification is shown (x5000).

Figure 3. Dynamic sintering curve for pure LAS (100LAS0SiC) and the 73LAS27SiC nanocomposite.

Figure 4. FE-SEM images of the fracture surface microstructure (secondary electron images) of sintered samples at (a) 1350 °C, (b) 1370 °C and (c) 1390 °C. Image

(d) (back scattered electron image) correspond to the polished surface of 1390 °C sintered sample.

Figure 5. XRD patterns of the LAS-nSiC starting material and the sintered LAS-nSiC composite at 1390 °C. Arrows mark the most important SiC peaks in pattern.

Figure 6. MT-DATA calculation for the mass amount of liquid phase formed for the LAS composition 1:1.009:3.109 with increasing temperature. Curve labelled 1 correspond to the liquid phase.

Figure 7. Expansion versus temperature of the LAS-nSiC sintered at different temperatures.

Figure 1
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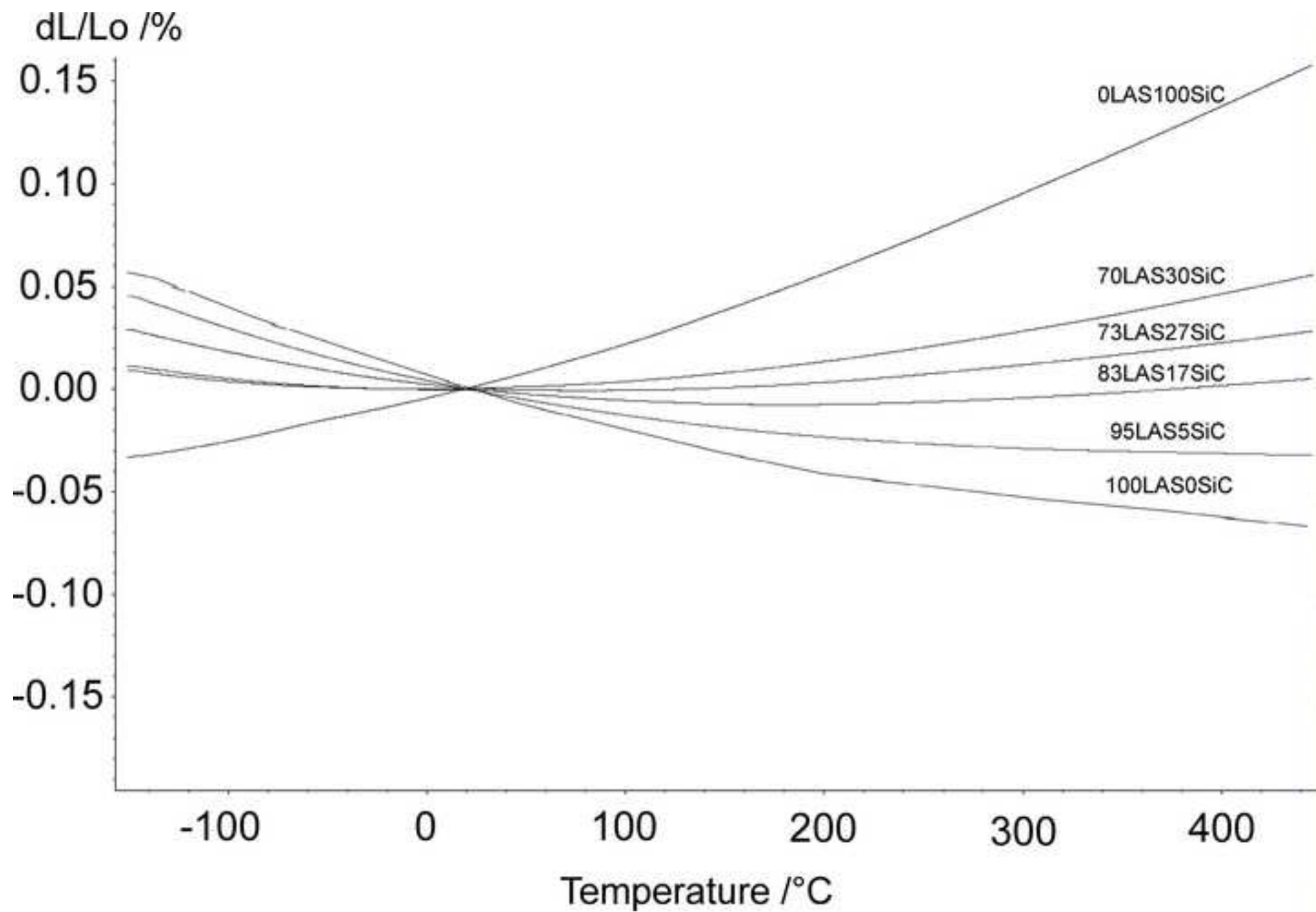


Figure 2
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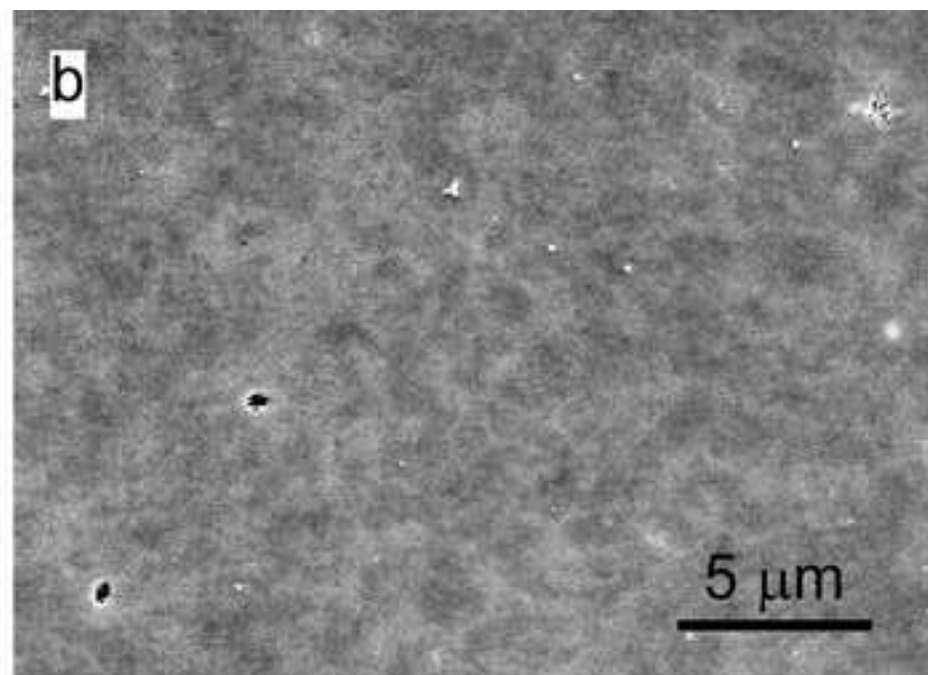
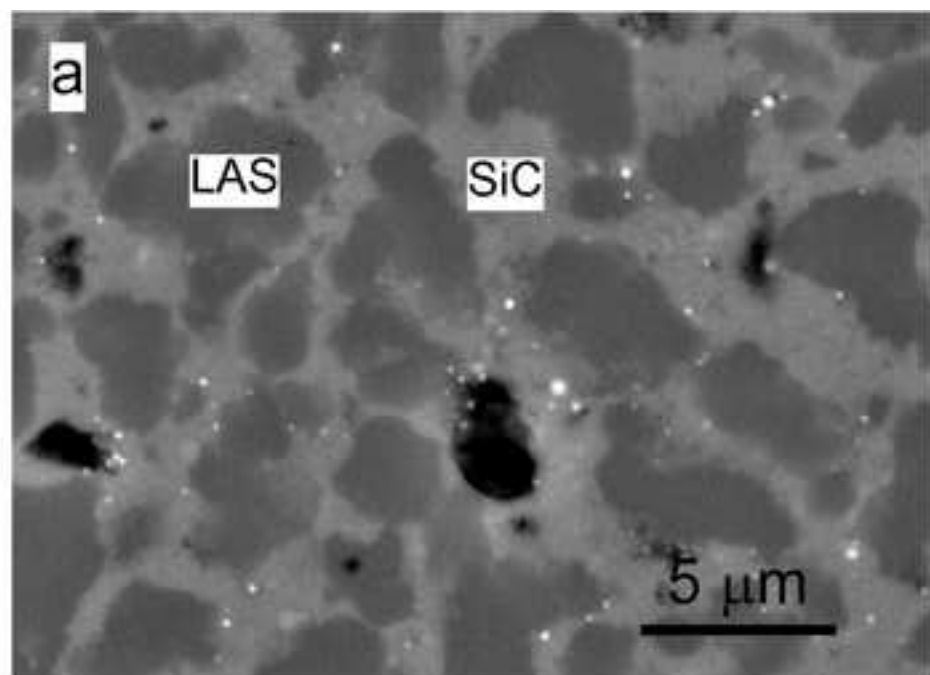


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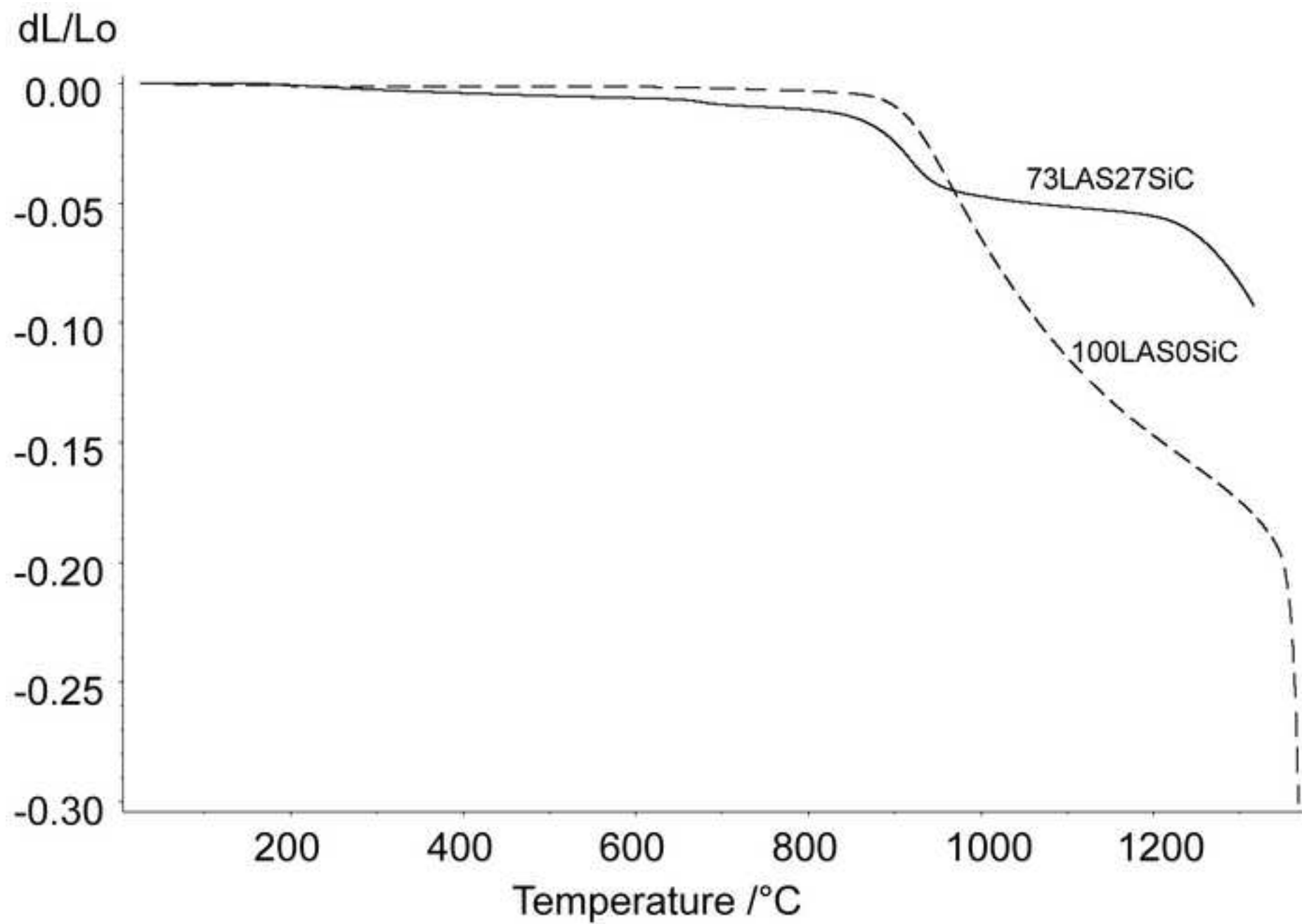


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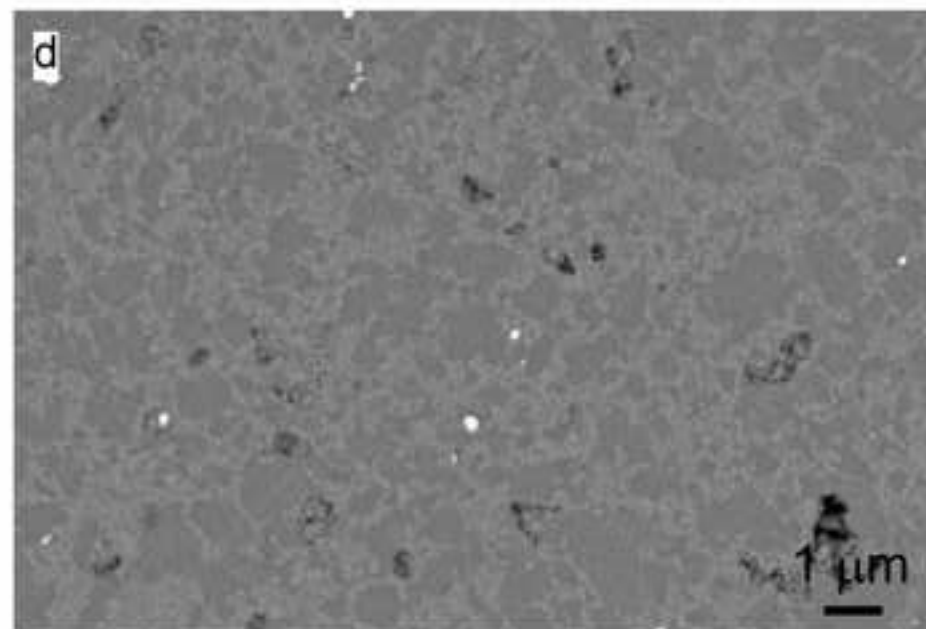
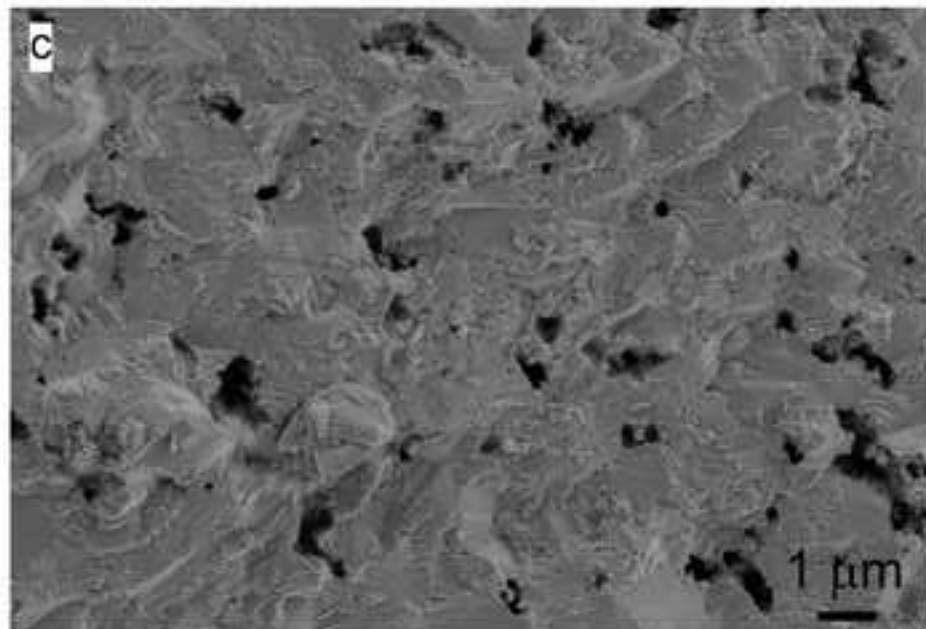
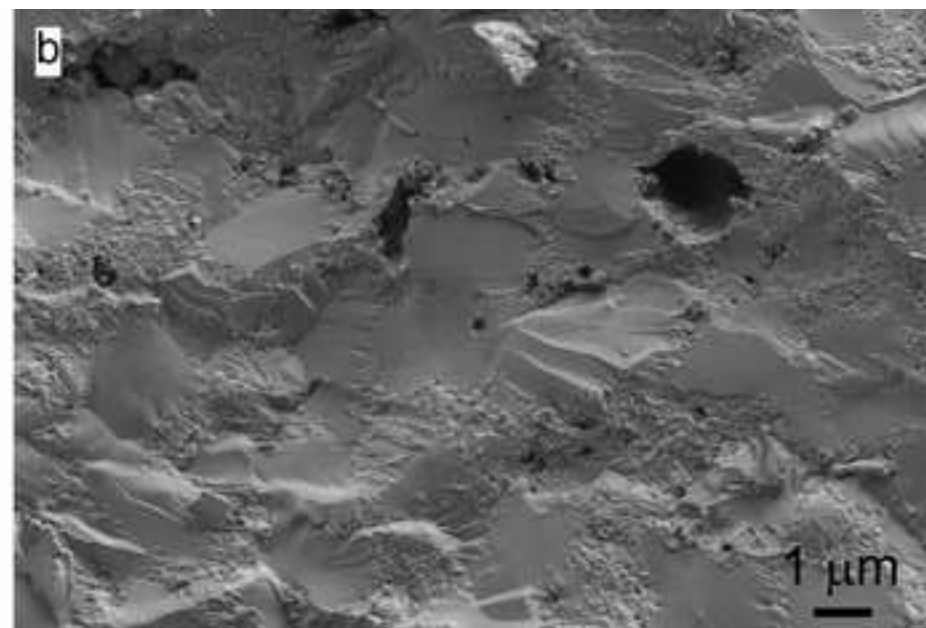
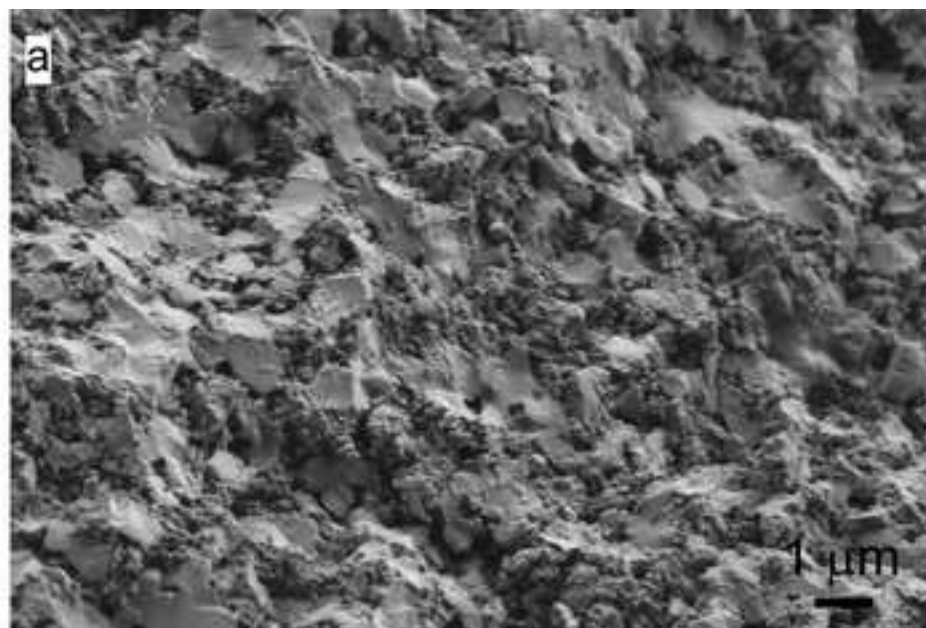


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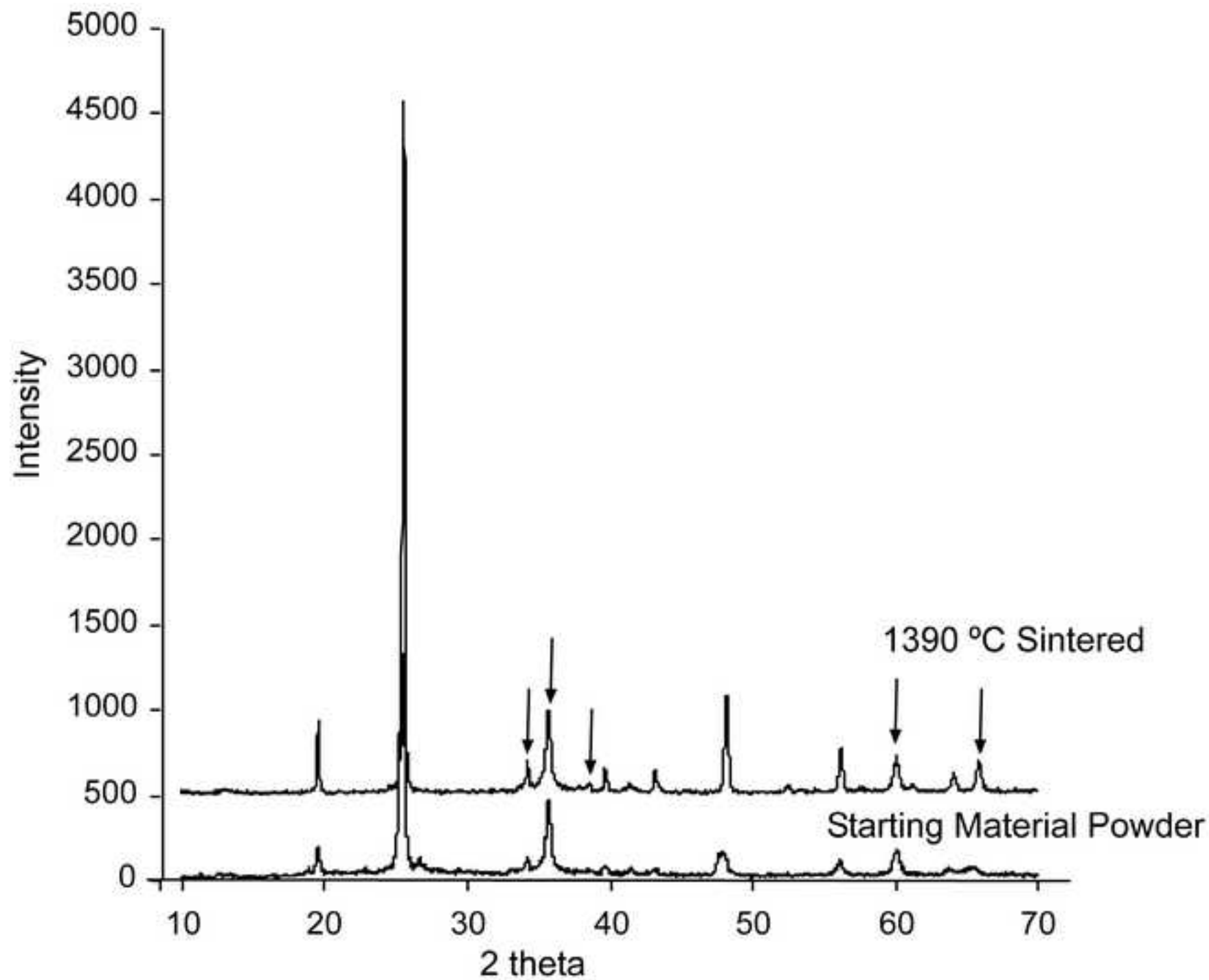


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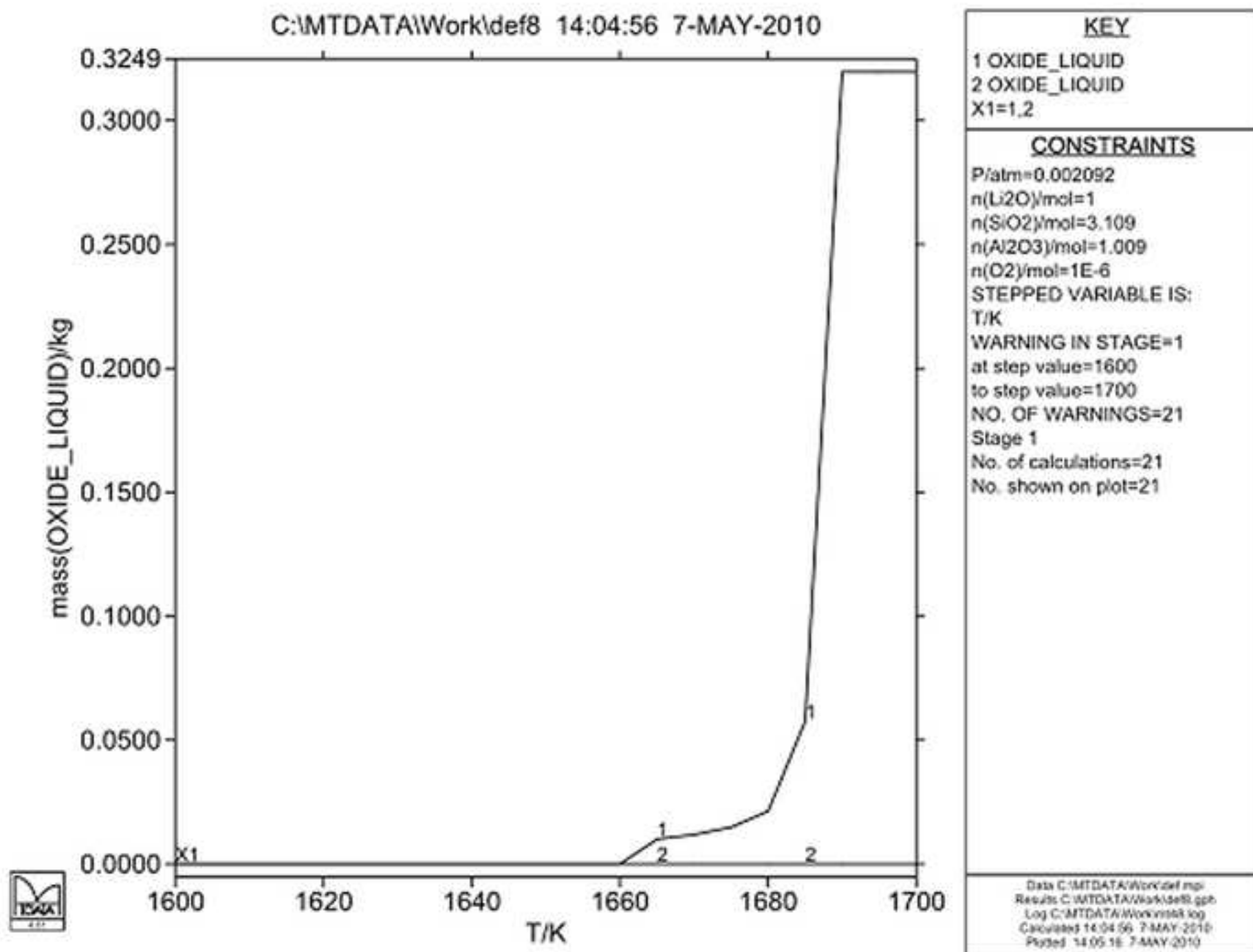


Figure 7
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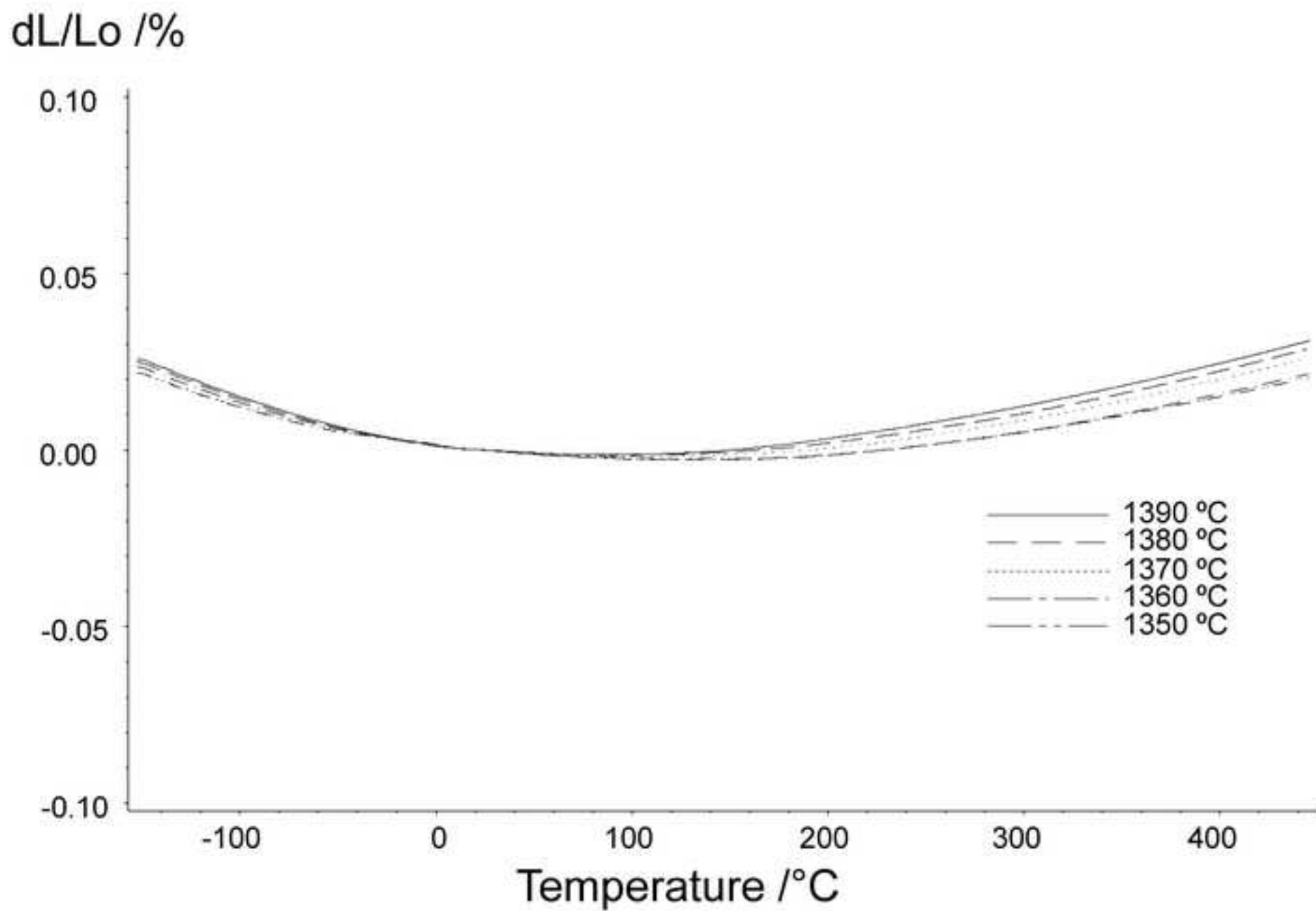


Table 1. Results of the sintered samples.

T (°C)	E (GPa)	σ_f (MPa)	Density (% t.d)	α -150 to 450 °C
1350	64.0±0.3	69.9±0.8	77.02±0.3	-0.02 x10 ⁻⁶
1360	67.8±0.2	85.1±0.3	80.24±0.2	-0.03 x10 ⁻⁶
1370	79.9±0.3	90.8±0.3	83.87±0.4	0.07 x10 ⁻⁶
1380	106.4±0.4	114.6±0.4	93.55±0.5	0.07 x10 ⁻⁶
1390	105.0±0.3	114.9±0.3	95.56±0.2	0.09 x10 ⁻⁶